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(54) [Title of the Invention]

ORGANIC ELECTROLUMINESCENCE ELEMENT AND METHOD FOR  
MANUFACTURING THE SAME

(57) [Abstract]

30 [Problem] To provide an organic EL element with a low driving voltage and high light emission

luminance, and a method for manufacturing the same.

[Solution] An organic electroluminescence element has an organic light emitting layer sandwiched between an anode layer and a cathode layer, wherein an organic semiconductor layer is provided between the anode layer and the cathode layer, and an inorganic charge-barrier layer is provided on one or both sides of the organic light emitting layer.

[Scope of Claim]

[Claim 1] An organic electroluminescence element comprising an organic light emitting layer sandwiched between an anode layer and a cathode layer,

characterized in that an organic semiconductor layer is further provided between the anode layer and the cathode layer; and

an inorganic charge-barrier layer is provided on one or both sides of the organic light emitting layer.

[Claim 2] The organic electroluminescence element according to claim 1, characterized in that a resistivity of the organic semiconductor layer ranges from  $1 \times 10^{-1}$  to  $1 \times 10^9 \Omega\cdot\text{cm}$ .

[Claim 3] The organic electroluminescence element according to claim 1 or 2, characterized in that a thickness of the organic semiconductor layer ranges from 0.1 to 500 nm.

[Claim 4] The organic electroluminescence element according to any one of claims 1 to 3, characterized in that the organic semiconductor layer is a combination of an organic compound and an oxidizing dopant, a combination of an organic compound and a reducing dopant, or a combination of an organic compound and a conductive particle.

[Claim 5] The organic electroluminescence element according to any one of claims 1 to 4, characterized in that the inorganic charge-barrier layer provided between the anode layer and the organic light emitting layer is at least one inorganic compound selected from a group consisting of silicon oxide, ZnO, GaN, InGaN, p-type  $a\text{-Si}_{1-x}\text{C}_x$  ( $0.5 < x < 1$ ),  $a\text{-Si}_{1-x}\text{N}_x$  ( $0.4 < x < 1$ ), and diamond like carbon, or a combination of at least one compound selected from the following

group A and at least one compound selected from the following group B.

group A: chalcogenide or nitride of Si, Ge, Sn, Pb, Ga, In, Zn, Cd, and Mg

group B: compound belonging to Groups 5A to 8 of the periodic table

- 5 [Claim 6] The organic electroluminescence element according to any one of claims 1 to 5, characterized in that the inorganic charge-barrier layer provided between the cathode layer and the organic light emitting layer is at least one inorganic compound selected from a group consisting of chalcogenide of alkali metal, chalcogenide of alkaline earth metal, halide of alkali metal, and halide of alkaline earth metal.

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[Claim 7] The organic electroluminescence element according to any one of claims 1 to 6, characterized in that the inorganic charge-barrier layer provided between the cathode layer and the organic light emitting layer is at least one inorganic compound selected from a group consisting of  $\text{Li}_2\text{O}$ ,  $\text{LiF}$ ,  $\text{CsF}$ ,  $\text{Cs}_2\text{O}$ ,  $\text{LiCl}$ ,  $\text{BaO}$ ,  $\text{SrO}$ ,  $\text{MgO}$ ,  $\text{MgF}_2$ ,  $\text{SrCl}_2$ , n-type a-SiC, and  
15 n-type a-Si<sub>1-x</sub>N<sub>x</sub> ( $0.1 < x < 0.7$ ).

[Claim 8] The organic electroluminescence element according to any one of claims 1 to 7, characterized in that a thickness of the inorganic charge-barrier layer ranges from 1 to 1000 nm.

- 20 [Claim 9] The organic electroluminescence element according to any one of claims 1 to 8, characterized in that the following condition is satisfied if the organic light emitting layer has an electron mobility of  $\mu_e$  and a hole mobility of  $\mu_h$ .

$$\mu_h > \mu_e > \mu_h/1000$$

- 25 [Claim 10] A method for manufacturing the organic electroluminescence element according to any one of claims 1 to 9, characterized by comprising a step of forming the organic semiconductor layer and the inorganic charge-barrier layer by an evaporation method or a sputtering method between the anode layer and the organic light emitting layer and/or between the cathode layer and the organic light emitting layer.

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[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The invention relates to an organic electroluminescence element (hereinafter also referred to as “an organic EL element”). More specifically, the invention relates to an organic EL element that is preferably used for a household or industrial display device (display), a light source of a printer head, or the like.

[0002]

[Prior Art] An example of a conventional organic EL element is disclosed in, for example, US Patent No. 5,853,905. As shown in FIG. 5, the organic EL element 40 is constituted by an anode 30, a first insulating layer 32, an organic light emitting layer 34, a second insulating layer 36, and a cathode 38 in order to improve the efficiency of light emission and durability. The first insulating layer 32 and the second insulating layer 36 are provided in order to serve an electron-barrier function and a hole-barrier function respectively. In addition, the first and second insulating layers 32 and 36 are formed to have a thickness that allows charges to be injected from the anode 30 and the cathode 38 by a tunnel effect, respectively.

[0003] Further, an organic EL element 60 as shown in FIG. 6 is disclosed in Japanese Patent Laid-Open No. Hei 4-297076, where organic film stacked layers of three-layer organic films 52, 54, and 56 are sandwiched between a cathode layer 58 and an anode layer 50 as a transparent electrode. The organic EL element 60 is intended to confine carriers in the light emitting layer 56 using the first and second organic films 52 and 54, so that high light emission luminance (light emission efficiency) is obtained at a low driving voltage. Accordingly, among the three-layer organic films 52, 54, and 56, the first organic film 52 in contact with the cathode layer 58 is doped with a donor impurity, the second organic film 54 in contact with the anode layer 50 is doped with an acceptor impurity, and the light emitting layer 56 is formed as an intermediate layer. Further, a difference in electron affinity between the first organic layer 52 doped with a donor impurity and the organic light emitting layer is set to 0.5 eV or more.

[0004] On the other hand, the applicant of the invention has suggested in Japanese Patent

Laid-Open No. Hei 3-77299 an organic EL element that can be driven at a low voltage while emitting light with high luminance. This organic EL element is specifically constituted by an anode, an inorganic amorphous hole injection/transporting layer, an electron-barrier layer, a light emitting layer, and a cathode; a cathode, a light emitting layer, a hole-barrier layer, an inorganic amorphous electron injection/transporting layer, and a cathode; or an anode, an inorganic amorphous hole injection/transporting layer, an electron-barrier layer, a light emitting layer, a hole-barrier layer, an inorganic amorphous electron injection/transporting layer, and a cathode.

[0005]

[Problems to be Solved by the Invention] However, the organic EL element disclosed in US Patent No. 5,853,905 has a problem that a driving voltage is high. Meanwhile, the organic EL element disclosed in Japanese Patent Laid-Open No. Hei 4-297076 has a problem that carrier confinement effect and durability are not improved since the first and second organic films 52 and 54 function as electron-barrier layers. In addition, a CN-substituted compound or a quinone compound used as an acceptor impurity in the second organic film 54 tends to react with the compound contained in the first and second organic films 52 and 54 and easily form a charge transfer complex or an excited complex (exciplex), which causes a problem of reduced light emission luminance or low durability of the organic EL element. Further, the difference in electron affinity between the first organic layer and the organic light emitting layer makes a blocking junction between the organic light emitting layer and the first organic layer, which often causes a problem of poor electron injection properties from the first organic layer to the organic light emitting layer.

[0006] Moreover, the organic EL element suggested in Japanese Patent Laid-Open No. Hei 3-77299, which can be driven at a low voltage of 5 V or less and emit light with high luminance, requires a specific manufacturing apparatus such as a plasma CVD when forming the inorganic amorphous hole injection/transporting layer and the inorganic amorphous electron injection/transporting layer.

[0007] Thus, the inventor of the invention and others have been dedicated to examining the

foregoing problems, and have found that high light emission luminance can be obtained at a low driving voltage by providing an organic semiconductor layer together with an inorganic charge-barrier layer. That is to say, it is an object of the invention to provide an organic EL element that is manufactured easily, driven at a low voltage, and has high light emission luminance, as well as a method for manufacturing such an organic EL element efficiently.

[0008]

[Means for Solving the Problems] According to a mode of an organic EL element of the invention, the organic EL element has an organic light emitting layer sandwiched between an anode layer and a cathode layer, and is characterized in that an organic semiconductor layer is provided between the anode layer and the cathode layer, and an inorganic charge-barrier layer is provided on one or both sides of the organic light emitting layer. According to such a structure, the organic light emitting layer is not in direct contact with the anode layer or the cathode layer since the organic semiconductor layer is sandwiched therebetween. Therefore, hole and electron injection properties are improved, and the organic EL element is easily driven at a low voltage. Further, the inorganic charge-barrier layer, which is in contact with the organic light emitting layer, has high durability, and does not influence the organic light emitting layer, can provide an excellent charge confinement effect, improve the durability of the organic EL element, and increase light emission luminance.

[0009] In addition, the organic EL element of the invention is preferably formed so that the resistivity of the organic semiconductor layer ranges from  $1 \times 10^{-1}$  to  $1 \times 10^9 \Omega\text{-cm}$ . According to such a structure, the hole and electron injection properties are further improved, and the organic EL element is easily driven at a low voltage.

[0010] In addition, the organic EL element of the invention is preferably formed so that the thickness of the organic semiconductor layer ranges from 0.1 to 500 nm. According to such a structure, hole and electron injection properties are further improved, and the organic EL element is easily driven at a low voltage.

[0011] In addition, the organic EL element of the invention is preferably formed so that the organic semiconductor layer is a combination of an organic compound and an oxidizing dopant, a combination of an organic compound and a reducing dopant, or a combination of an organic compound and a conductive particle. According to such a structure, hole injection properties of the anode layer and electron injection properties of the cathode layer are further improved, and the organic EL element is easily driven at a low voltage.

[0012] In addition, the organic EL element of the invention is preferably formed so that the inorganic charge-barrier layer provided between the anode layer and the organic light emitting layer is at least one inorganic compound selected from a group consisting of silicon oxide, ZnO, GaN, InGaN, p-type a-Si<sub>1-x</sub>C<sub>x</sub> (0.5 < x < 1), and a-Si<sub>1-x</sub>N<sub>x</sub> (0.47 < x < 0.57), or a combination of at least one compound selected from group A and at least one compound selected from group B.  
group A: chalcogenide or nitride of Si, Ge, Sn, Pb, Ga, In, Zn, Cd, and Mg  
group B: compound belonging to Groups 5A to 8 of the periodic table

According to such a structure, a superior charge confinement effect can be obtained and the durability of the organic EL element is further improved.

[0013] In addition, the organic EL element of the invention is preferably formed so that the inorganic charge-barrier layer provided between the cathode layer and the organic light emitting layer is at least one inorganic compound selected from a group consisting of chalcogenide of alkali metal, chalcogenide of alkaline earth metal, halide of alkali metal, and halide of alkaline earth metal.

[0014] In addition, the organic EL element of the invention is preferably formed so that the inorganic charge-barrier layer provided between the cathode layer and the organic light emitting layer is a combination of at least one compound selected from at least one inorganic compound selected from a group consisting of Li<sub>2</sub>O, LiF, CsF, Cs<sub>2</sub>O, LiCl, BaO, SrO, MgO, MgF<sub>2</sub>, SrCl<sub>2</sub>, n-type a-SiC, and a-Si<sub>1-x</sub>N<sub>x</sub> (0.47 < x < 0.57). According to such a structure, a superior hole confinement effect can be obtained and the durability of the organic EL element is further improved.

[0015] In addition, the organic EL element of the invention is preferably formed so that the thickness of the inorganic charge-barrier layer ranges from 1 to 1000 nm. According to such a structure, a superior charge confinement effect can be obtained and the durability of the organic EL element is further improved.

[0016] In addition, the organic EL element of the invention is preferably formed so that the following condition is satisfied if the organic light emitting layer has an electron mobility of  $\mu_e$  and a hole mobility of  $\mu_h$ .

$$\mu_h > \mu_e > \mu_h/1000$$

According to such a structure, electrons and holes can be recombined efficiently in the organic light emitting layer, and high light emission luminance can be obtained even when a low voltage is applied. Note that the electron mobility ( $\mu_e$ ) and the hole mobility ( $\mu_h$ ) of an organic light emitting material can be measured by a time of flight (TOF) method under the condition where a DC voltage of  $1 \times 10^4$  to  $1 \times 10^6$  V/cm·s is applied.

[0017] In addition, another mode of the invention is a method for manufacturing an organic EL element, which is characterized by having a step of forming an organic semiconductor layer and an inorganic charge-barrier layer by an evaporation method or a sputtering method between an anode layer and an organic light emitting layer and/or between a cathode layer and the organic light emitting layer. According to such a mode, a large area can be formed to have an even thickness, a manufacturing apparatus is simplified as a whole, and thus an inexpensive organic EL element can be obtained.

[0018]

[Embodiment Modes of the invention] Embodiment Modes of the invention are described below with reference to drawings. Note that the reference drawings only schematically show the size, shape, and arrangement relationship of each component so that the invention is understood. Therefore, the invention is not limited to the examples shown in the drawings. Further, in the drawings, hatching indicating a cross section is omitted in some cases.

[0019] [Embodiment Mode 1] First, Embodiment Mode 1 of the organic EL element of the invention is described with reference to FIG. 1. FIG. 1 is a cross sectional view of an organic EL element 100 having a structure where an anode layer 10, a first organic semiconductor layer 12, a first inorganic charge-barrier layer 14, an organic light emitting layer 16, a second inorganic charge-barrier layer 18, a second organic semiconductor layer 20, and a cathode layer 22 are stacked in this order over a substrate (not shown). Mainly described below are the organic light emitting layer 16, the first and second organic semiconductor layers 12 and 18, and the first and second inorganic charge-barrier layers 14 and 20, which illustrate some features of Embodiment Mode 1. Accordingly, structures and manufacturing methods of other components such as the anode layer 10 and the cathode layer 22 are described simply since a general structure can be applied.

[0020] (1) Organic light emitting layer

(organic light emitting substance) An organic light emitting substance used as a constituent material of an organic light emitting layer preferably has the following three functions.

(a) Charge injection function: a function of injecting holes from an anode or a hole injection layer when an electric field is applied, while injecting electrons from a cathode layer or an electron injection layer.

(b) Transporting function: a function of transporting injected holes and electrons by the electric field force.

(c) Light emitting function: a function of offering a place for electrons and holes to be recombined so as to emit light.

However, not all the above functions (a) to (c) are required to be provided. For example, some substances of which hole injection/transporting properties are much better than electron injection/transporting properties are preferably used as an organic light emitting material. Therefore, in the invention, the organic light emitting layer is preferably made of an organic light emitting substance including a styryl group (also referred to as an aromatic ring compound in some cases), which is represented by the following general formulas (1) to (3),. Note that a styryl group represented by the following general formula (4) is preferably used as the styryl

group included in the general formulas (1) to (3).

[0021]

[Chemical Formula 1]

5

[0022] [In the general formula (1), Ar<sup>1</sup> is an aromatic group with 6 to 40 carbons, Ar<sup>2</sup>, Ar<sup>3</sup>, and Ar<sup>4</sup> each are an aromatic group with 6 to 40 hydrogen atoms or carbons, at least one of which is an aromatic group, and condensation number n is an integer of 1 to 6.]

10 [0023]

[Chemical Formula 2]

[0024] [In the general formula (2), Ar<sup>5</sup> is an aromatic group with 6 to 40 carbons, Ar<sup>6</sup> and Ar<sup>7</sup> each are an aromatic group with 6 to 40 hydrogen atoms or carbons, at least one of Ar<sup>5</sup>, Ar<sup>6</sup>, and

15 Ar<sup>7</sup> is substituted by a styryl group, and condensation number m is an integer of 1 to 6.]

[0025]

[Chemical Formula 3]

20 [0026] [In the general formula (3), Ar<sup>9</sup> to Ar<sup>13</sup> each are an aromatic group with 6 to 40 carbons, Ar<sup>8</sup> and Ar<sup>14</sup> each are an aromatic group with 6 to 40 hydrogen atoms or carbons, at least one of Ar<sup>8</sup> to Ar<sup>14</sup> is substituted by a styryl group, and condensation numbers p, q, r, and s each are 0 or 1.]

25 [0027]

[Chemical Formula 4]

[0028] [In the general formula (4), Ar<sup>15</sup>, Ar<sup>16</sup>, and Ar<sup>17</sup> each are an aromatic group with 6 to 40 hydrogen atoms or carbons.]

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[0029] In addition, as a preferable aryl group with 5 to 40 nuclear atoms among aromatic groups with 6 to 40 carbons contained in the organic light emitting substance represented by the general formulas (1) to (3), there are phenyl, naphthyl, anthranyl, phenanthryl, pyrenyl, crycenyl, coronyl, biphenyl, terphenyl, pyrrolyl, furanyl, thiophenyl, benzothiophenyl, oxadiazolyl, 5 diphenylanthranyl, indolyl, carbazolyl, pyridyl, benzoquinolyl, and the like.

[0030] Note that the aromatic group with 6 to 40 carbons may be further substituted by a substituent, and as a preferable substituent, there are an alkyl group with 1 to 6 carbons (ethyl group, methyl group, i-propyl group, n-propyl group, s-butyl group, t-butyl group, pentyl group, 10 hexyl group, cyclopentyl group, cyclohexyl group, or the like), an alkoxy group with 1 to 6 carbons (ethoxy group, methoxy group, i-propoxy group, n-propoxy group, s-butoxy group, t-butoxy group, pentoxy group, hexyloxy group, cyclopentoxy group, cyclohexyloxy group, or the like), an aryl group with 5 to 40 nuclear atoms, an amino group substituted by an aryl group with 5 to 40 nuclear atoms, an ester group having an aryl group with 5 to 40 nuclear atoms, an 15 ester group having an alkyl group with 1 to 6 carbons, a cyano group, a nitro group, and a halogen atom.

[0031] In addition, as a preferable arylene group with 5 to 40 nuclear atoms in the organic light emitting substance represented by the formulas (1) to (3), there are phenylene, naphthylene, 20 anthranylene, phenanthrylene, pyrenylene, crycenylene, coronylene, biphenylene, terphenylene, pyrrolylene, furanylene, thiophenylene, benzothiophenylene, oxadiazolylene, diphenylanthranylene, indolylene, carbazolylene, pyridylene, benzoquinolylene, and the like.

[0032] In addition, the material of the organic light emitting layer is preferably combined with 25 a benzothiazole-, benzimidazole-, or benzoxazole-based fluorescent whitening agent, a styrylbenzene-based compound, or a metal complex having a 8-quinolinol derivative as a ligand. Further, the material of the organic light emitting layer is also preferably combined with an organic light emitting material having a distyrylarylene skeleton, for example a light emitting material using 4,4'-bis(2,2'-diphenylvinyl) biphenyl) or the like as a host material that is doped 30 with a blue to red strong fluorescent dye such as a coumarin-based dye or a fluorescent dye

similar to the host.

[0033] If an electron injection layer is provided between the cathode and the organic light emitting layer in order to obtain excellent adhesiveness, smoothly transport electrons to the organic light emitting layer, and improve mechanical strength, some of the constituent materials of the electron injection layer are preferably the same as the constituent materials of the organic light emitting layer. That is to say, the above-mentioned aromatic ring compound represented by the formulas (1) to (3) is preferably used for the organic light emitting layer and the electron injection layer. Note that when the electron injection layer is provided in the organic light emitting layer, the same kind of aromatic ring compound is preferably used. For example, the organic light emitting layer preferably contains not less than 50% by weight of the same kind of aromatic ring compound, and more preferably not less than 60% by weight.

[0034] (forming method) Next, a method for forming the organic light emitting layer is described. For example, a known method such as an evaporation method, a spin coating method, a casting method, and an LB method can be applied. In addition, the electron injection layer and the organic light emitting layer are preferably formed by the same method as described above. For example, when the electron injection layer is formed by an evaporation method, the organic light emitting layer is also preferably formed by the evaporation method.

[0035] In addition, the organic light emitting layer is preferably a molecule built-up such as a thin film formed by the deposition of a gas-phase material compound and a film formed by the solidification of a solution or liquid-phase material compound. In general, the molecule built-up can be differentiated from a thin film (molecule built-up film) formed by an LB method by differences in aggregation structure and higher-order structure, and a functional difference due to these differences. Moreover, the organic light emitting layer can also be formed by forming a thin film by a spin coating method using a solution that is obtained by dissolving an adhesive such as resin and an organic light emitting material in a solvent.

[0036] (thickness of organic light emitting layer) The thickness of the thus formed organic light

emitting layer is not specifically limited and can be appropriately selected depending on the situation, though it preferably ranges from 5 nm to 5  $\mu\text{m}$ . This is because light emission luminance may decrease when the thickness of the organic light emitting layer is less than 5 nm, while an applied voltage tends to increase when the thickness of the organic light emitting layer is more than 5  $\mu\text{m}$ . Accordingly, the thickness of the organic light emitting layer more preferably ranges from 10 nm to 3  $\mu\text{m}$ , and further preferably from 20 nm to 1  $\mu\text{m}$ .

#### [0037] (2) Organic semiconductor layer

The first and second organic semiconductor layers are provided to facilitate the hole and electron injection. That is to say, because of large energy barrier to hole injection and electron injection, it is difficult to inject holes and electrons even when the organic light emitting layer that is an insulating layer is brought into direct contact with the anode layer and the cathode layer. Meanwhile, when the first and second organic semiconductor layers are provided, energy barrier to hole injection and electron injection can be reduced. Thus, holes and electrons can be easily injected, leading to a low driving voltage, for example 10 V or less. In addition, these organic semiconductor layers can be easily formed without using a plasma CVD apparatus or the like, but using a vacuum evaporation apparatus, a thermal CVD apparatus, or the like, which has a relatively simple structure. Therefore, providing the organic semiconductor layers is advantageous in manufacturing as compared with the case of providing inorganic semiconductor layers.

#### [0038] 1. Constituent material

The organic semiconductor layer is preferably a combination of an organic compound and an oxidizing dopant, a combination of an organic compound and a reducing dopant, or a combination of an organic compound and a conductive particle.

[0039] Specifically, as a preferable combination of an organic compound and a conductive particle, there is a material where a conductive metal particle or a conductive inorganic particle is mixed and dispersed in an organic compound that is generally used for an organic EL element, such as polyvinylcarbazole, polyaniline, polystyrene, amine derivative, porphyrin, and

phthalocyanines. In addition, as types of conductive particles, there are one or a combination of two or more of gold, silver, copper, nickel, solder, aluminum, indium oxide, tin oxide, zinc oxide, and the like. In addition, the conductive metal particle preferably has an average grain diameter of 0.001 to 1  $\mu\text{m}$ . Moreover, the conductive particle is preferably added at 0.1 to 50 parts by weight relative to 100 parts by weight of organic compound.

[0040] In addition, as a combination of an organic compound and an oxidizing dopant, an organic compound such as polyvinylcarbazole, polyaniline, polycarbonate or polyether containing amine in the main chain, polysulfone, porphyrin, and copper phthalocyanine may be combined with an oxidizing dopant such as quinone derivative, metal halide, Lewis acid, organic acid, metal halide salt, Lewis acid salt, fullerenes, and organic acid salt. Accordingly, as a more specific combination of an organic compound and an oxidizing dopant, there are polyvinylcarbazole and antimony chloride, polyaniline and antimony chloride, amine derivative and C60, NPD and thioketone, porphyrin and TCNQ, copper phthalocyanine and TCNE, amine oligomer and DDQ, amine dendrimer and DDQ, and the like.

[0041] Note that when an organic compound is combined with an oxidizing dopant, the addition ratio to the organic compound preferably ranges from 1 : 1 to 20 : 1 (molar ratio). This is because the light emission luminance of the organic EL element may decrease or the life thereof is shortened when the addition ratio of the oxidizing dopant to the organic compound is out of this range. Accordingly, the addition ratio of the oxidizing dopant to the organic compound more preferably ranges from 1 : 1 to 10 : 1 (molar ratio), and further preferably from 1 : 1 to 5 : 1.

[0042] In addition, as a combination of an organic compound and a reducing dopant, an organic compound such as Alq, DPAVBi, and PBD is preferably combined with at least one reducing dopant selected from a group consisting of alkali metal, alkaline earth metal, rare earth metal, oxide of alkali metal, halide of alkali metal, oxide of alkaline earth metal, halide of alkaline earth metal, oxide of rare earth metal, and halide of rare earth metal. Further, the amount of the added reducing dopant can be equal to the addition ratio of the oxidizing dopant to the organic

compound. Note that the organic compound preferably has superior electron transporting properties, and the alkali metal is preferably Cs and Li.

[0043] The above-mentioned combination of an organic compound and an oxidizing dopant, combination of an organic compound and a reducing dopant, or combination of an organic compound and a conductive particle can be suitably used for each of the first and second organic semiconductor layers. However, the combination of an organic compound and an oxidizing dopant, or the combination of an organic compound and a conductive particle is more preferably used for the first organic semiconductor layer in order to further improve hole injection properties. In addition, the combination of an organic compound and a reducing dopant, or the combination of an organic compound and a conductive particle is more preferably used for the second organic semiconductor layer in order to further improve electron injection properties.

#### [0044] 2. Resistivity

The resistivity of the first and second organic semiconductor layers preferably ranges from  $1 \times 10^{-1}$  to  $1 \times 10^9 \Omega\cdot\text{cm}$ . This is because adjacent organic EL elements may be short-circuited when the resistivity is less than  $1 \times 10^{-1} \Omega\cdot\text{cm}$ , while hole and electron injection properties may decrease when the resistivity is more than  $1 \times 10^9 \Omega\cdot\text{cm}$ . Accordingly, the resistivity of the first and second organic semiconductor layers more preferably ranges from  $1 \times 10^1$  to  $1 \times 10^8 \Omega\cdot\text{cm}$ , and further preferably from  $1 \times 10^2$  to  $1 \times 10^7 \Omega\cdot\text{cm}$ .

#### [0045] 3. Thickness

The thickness of the first and second organic semiconductor layers preferably ranges from 1 to 1000 nm. This is because mechanical strength may decrease or hole and electron injection properties may decrease when the thickness is less than 1 nm, while improvement in hole and electron injection properties may decrease on the contrary or deposition time may significantly increase when the thickness is more than 1000 nm. Accordingly, the thickness of the first and second organic semiconductor layers more preferably ranges from 10 to 200 nm.

#### [0046] (3) Inorganic charge-barrier layer

The first and second inorganic charge-barrier layers are provided to facilitate hole and electron confinement injection properties. That is to say, the first inorganic charge-barrier layer is an electron-barrier layer and provided on the anode side so as to be in contact with the organic light emitting layer. Thus, the first inorganic charge-barrier layer can energetically block electrons that attempt to pass through the organic light emitting layer, so that the electrons can be efficiently confined in the organic light emitting layer. Meanwhile, the second inorganic charge-barrier layer is a hole-barrier layer and provided on the cathode side so as to be in contact with the organic light emitting layer. Thus, the second inorganic charge-barrier layer can energetically block holes that attempt to pass through the organic light emitting layer, so that the holes can be efficiently confined in the organic light emitting layer. As a result, the first and second inorganic charge-barrier layers allow the electrons and holes confined in the organic light emitting layer to be recombined efficiently, leading to improved light emission efficiency. Note that even when the first and second inorganic charge-barrier layers are provided, the first inorganic charge-barrier layer rarely blocks holes energetically, which are transported from the anode layer, and similarly, the second inorganic charge-barrier layer rarely blocks electrons energetically, which are transported from the cathode layer.

[0047] 1. Constituent material

(first inorganic charge-barrier layer) The first inorganic charge-barrier layer provided between the anode layer and the organic light emitting layer is preferably at least one inorganic compound selected from a group consisting of silicon oxide, ZnO, GaN, InGaN, p-type a-Si<sub>1-x</sub>C<sub>x</sub> (0.5 < x < 1), and a-Si<sub>1-x</sub>N<sub>x</sub> (0.4 < x < 1), or the second inorganic charge-barrier layer provided between the cathode layer and the organic light emitting layer is preferably a combination of at least one compound selected from group A and at least one compound selected from group B.

group A: chalcogenide or nitride of Si, Ge, Sn, Pb, Ga, In, Zn, Cd, and Mg

group B: compound belonging to Groups 5A to 8 of the periodic table

By using such inorganic compounds, superior electron confinement effect can be obtained and the durability of the organic EL element is further improved. In addition, such inorganic compounds do not react with the constituent materials of the organic light emitting layer, and thus the use of the constituent materials of the organic light emitting layer is not limited to a

specific range.

[0048] (second inorganic charge-barrier layer)

By using such a combination of inorganic compounds, superior hole confinement effect can be  
5 obtained and the durability of the organic EL element is further improved.

[0049] The second inorganic charge-barrier layer is preferably made of at least one inorganic  
compound selected from a group consisting of  $\text{Li}_2\text{O}$ ,  $\text{LiF}$ ,  $\text{CsF}$ ,  $\text{Cs}_2\text{O}$ ,  $\text{LiCl}$ ,  $\text{BaO}$ ,  $\text{SrO}$ ,  $\text{MgO}$ ,  
10  $\text{MgF}_2$ ,  $\text{SrCl}_2$ , n-type a-SiC, and n-type a- $\text{Si}_{1-x}\text{N}_x$  ( $0.1 < x < 0.7$ ). By using such inorganic  
compounds, superior hole confinement effect can be obtained and the durability of the organic  
EL element is further improved. In addition, such inorganic compounds do not react with the  
constituent materials of the organic light emitting layer, and thus the use of the constituent  
materials of the organic light emitting layer is not limited to a specific range.

15 [0050] 2. Thickness

The thickness of the first and second inorganic charge-barrier layers preferably ranges from 1 to  
1000 nm. This is because mechanical strength may decrease or hole and electron confinement  
properties may decrease when the thickness is less than 1 nm, while improvement in hole and  
electron injection properties may also decrease or deposition time may significantly increase  
20 when the thickness is more than 1000 nm. Accordingly, the thickness of the first and second  
inorganic charge-barrier layers more preferably ranges from 10 to 200 nm.

[0051] (4) Electrode

(anode layer) For the anode layer, a metal, an alloy, or an electric conductive compound having a  
25 high work function (for example, 4.0 eV or more), or a mixture thereof is preferably used.  
Specifically, one or a combination of two or more of indium tin oxide (ITO), indium zinc oxide,  
tin, zinc oxide, gold, platinum, palladium, and the like can be used.

[0052] The thickness of the anode layer is also not specifically limited, though it preferably  
30 ranges from 10 to 1000 nm, and more preferably 10 to 200 nm. In addition, it is preferable that

the anode layer be substantially transparent, more specifically have a light transmittance of 10% or more, in order to efficiently extract light emitted from the organic light emitting layer to the outside.

5 [0053] (cathode layer) On the other hand, for the cathode layer, a metal, an alloy, or an electric conductive compound each having a low work function (for example, less than 4.0 eV), or a mixture thereof is preferably used. Specifically, one or a combination of two or more of magnesium, aluminum, indium, lithium, sodium, silver, and the like can be used. The thickness of the cathode layer is also not specifically limited, though it preferably ranges from 10 to 1000  
10 nm, and more preferably 10 to 200 nm.

[0054] [Embodiment Mode 2] An organic EL element 102 described in Embodiment Mode 2 has a structure where the anode layer 10, the first organic semiconductor layer 12, the first inorganic charge-barrier layer 14, the organic light emitting layer 16, an electron injection layer 24, and the  
15 cathode layer 22 are stacked in this order over a substrate (not shown) as shown in FIG. 2. The organic EL element 102 in Embodiment Mode 2 is constituted by the electron injection layer 24 including an electron transporting compound and a reducing dopant. That is to say, in Embodiment Mode 2, the first organic semiconductor layer 12 improves hole injection properties while the electron injection layer 24 improves electron injection properties, and the first  
20 inorganic charge-barrier layer 14 imparts electron-barrier properties. Mainly described below is the electron injection layer 24 which illustrates a feature of Embodiment Mode 2. Structures and manufacturing methods of other components such as the anode layer 10 and the cathode layer 22 can be similar to those described in Embodiment Mode 1.

25 [0055] (1) Electron injection area

(electron transporting compound) As the electron transporting compound, various compounds can be used as long as they have a function of transporting electrons injected from the cathode to an organic light emitting medium. Specifically, an aromatic ring compound including an aromatic ring that does not contain a nitrogen atom (also simply referred to as a non-nitrogenous  
30 heterocyclic compound), and an organic compound containing a nitrogenous heterocyclic

compound (also simply referred to as a nitrogenous heterocyclic compound) can be given as an example.

[0056] 1. Non-nitrogenous heterocyclic compound

5 The non-nitrogenous heterocyclic compound is defined as a compound including an aromatic ring that contains carbon (C) and hydrogen (H), or a compound including an aromatic ring that contains carbon (C), hydrogen (H), and oxygen (O). However, a nitrogen atom may be contained in a molecule other than the aromatic ring, and it is preferable that aromatic rings each of which does not contain a nitrogen atom be bonded to each other by, for example, a nitrogen  
10 atom. In addition, an aromatic ring compound containing carbon and hydrogen, and an aromatic ring compound containing carbon, hydrogen, and oxygen may be used separately or in combination.

[0057] When such a non-nitrogenous heterocyclic compound is used in combination with a  
15 reducing dopant described later, excellent electron injection properties can be obtained and reaction with a constituent material of an adjacent light emitting area can be suppressed. In other words, the non-nitrogenous heterocyclic compound includes an aromatic ring containing carbon and hydrogen, or an aromatic ring containing carbon, hydrogen, and oxygen, and does not include a nitrogen-containing group such as a nitrogen-containing aromatic ring and an  
20 electron withdrawing group (for example, -CN group, -NO<sub>2</sub> group, amide group, or imide group). Accordingly, a charge transfer complex or an exciplex with low light emission efficiency can be effectively prevented from being generated at an interface between an electron injection area and a light emitting area.

25 [0058] As a preferable non-nitrogenous heterocyclic compound, there is an aromatic ring compound including at least one aromatic ring selected from a group consisting of anthracene, fluorene, perylene, pyrene, phenanthrene, chrysene, tetracene, rubrene, terphenylene, quaterphenylene, sexiphenylene, triphenylene, picene, coronel, diphenylanthracene, benz[a]anthracene, and binaphthalene. It is more preferable that the non-nitrogenous  
30 heterocyclic compound include an aromatic ring substituted by a styryl group, an aromatic ring

substituted by a distyryl group, or an aromatic ring substituted by a tristyryl group. Such an aromatic ring substituted by a styryl group (including a distyryl group and a tristyryl group, hereinafter the same applies) can further improve the light emission luminance and life of the organic EL element. As an aromatic ring compound including such a group substituted by a styryl group, an aromatic ring compound similar to the aromatic ring compounds represented by the formulas (1) to (3), which are used for an organic light emitting medium, can be given as an example.

[0059] 2. Nitrogenous heterocyclic compound

In addition, as an electron transporting compound, a nitrogenous heterocyclic compound can be given. Even in the case of using such a nitrogenous heterocyclic compound, by using a reducing dopant with a work function of 2.9 eV or less among the reducing dopants described below, reaction with an organic light emitting medium material can be effectively suppressed to obtain high light emission luminance.

[0060] Such a nitrogenous heterocyclic compound can be defined as a compound having a heterocyclic ring containing a nitrogen atom. Specifically, a nitrogen-containing complex and a nitrogen-containing ring compound can be given. As a preferable nitrogen-containing complex, there are a metal complex having an 8-quinolinol derivative as a ligand, a phthalocyanine derivative, and metal phthalocyanine. In addition, as a preferable nitrogen-containing ring compound, there are an oxidiazole derivative, a thiadiazole derivative, a triazole derivative, a quinoxaline derivative, a quinoline derivative, and the like. Further, as a nitrogenous heterocyclic compound, heterocyclic tetracarboxylic acid anhydride such as an anthrone derivative, a fluorenylimethane derivative, carbodiimide, and naphthaleneperylene is also preferably used.

[0061] (reducing dopant) The electron injection area in Embodiment Mode 2 is characterized by including a reducing dopant as well as an electron transporting compound.

[0062] 1. Type

The reducing dopant can be defined as a substance that can reduce oxidized aromatic ring compound. Therefore, types of reducing dopants are not specifically limited as long as they have certain reducing properties. However, it is preferable to use the same kind of reducing dopant as used for the organic semiconductor layer.

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[0063] More specifically, as a preferable alkali metal, Li (lithium, work function: 2.93 eV), Na (sodium, work function: 2.36 eV), K (potassium, work function: 2.3 eV), Rb (rubidium, work function: 2.16 eV), and Cs (cesium, work function: 1.95 eV) can be given as an example. Note that the work function values in parentheses are listed on Handbook of Chemistry (Basic II, p.493, The Chemical Society of Japan), and hereinafter the same applies. In addition, as a preferable alkaline earth metal, Ca (calcium, work function: 2.9 eV), Mg (magnesium, work function: 3.66 eV), Ba (barium, work function: 2.52 eV), and Sr (strontium, work function: 2.0 to 2.5 eV) can be given as an example. Note that the work function value of strontium is listed on Physics of Semiconductor Device (N.Y. Wiley, 1969, p.366). In addition, as a preferable rare earth metal, Yb (ytterbium, work function: 2.6 eV), Eu (europium, work function: 2.5 eV), Gd (gadolinium, work function: 3.1 eV), and Er (erbium, work function: 2.5 eV) can be given as an example.

[0064] Further, as a preferable alkali metal oxide, Li<sub>2</sub>O, LiO, and NaO can be given for example. In addition, as a preferable alkaline earth metal oxide, CaO, BaO, SrO, BeO, and MgO can be given for example. In addition, as a preferable alkali metal halide, fluorides such as LiF, NaF, and KF as well as LiCl, KCl, and NaCl can be given for example. In addition, as a preferable alkaline earth metal halide, fluorides such as CaF<sub>2</sub>, BaF<sub>2</sub>, SrF<sub>2</sub>, MgF<sub>2</sub>, and BeF<sub>2</sub>, and halides other than fluorides can be given for example. As a preferable rare earth halide, fluorides such as LaF<sub>3</sub>, YbF<sub>3</sub>, and EuF<sub>3</sub> can be given for example.

[0065] Further, as a preferable reducing dopant, an aromatic compound coordinated to alkali metal can also be given. The aromatic compound coordinated with alkali metal is represented by, for example, the following formula (5).

30  $A^+Ar^{20-} \dots$  (5)

In the formula (5), A represents alkali metal, and Ar<sup>20</sup> is an aromatic compound with 10 to 40 carbons. As the aromatic compound represented by the formula (5), for example, there are anthracene, naphthalene, diphenylanthracene, terphenyl, quaterphenyl, quinquephenyl, sexiphenyl, and derivatives of them.

5

[0066] 2. Amount of dopant

The amount of reducing dopant added to the electron injection area preferably ranges from 0.01 to 50% by weight when the whole material for the electron injection area is 100% by weight. When the amount of reducing dopant is less than 0.01% by weight, the light emission luminance  
10 of the organic EL element tends to decrease or the life thereof tends to be shortened. On the other hand, when the amount of reducing dopant is more than 50% by weight, the light emission luminance tends to decrease or the life thereof tends to be shortened similarly. Accordingly, the amount of reducing dopant more preferably ranges from 0.2 to 20% by weight in order to achieve a better balance between the light emission luminance and the life.

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[0067] In addition, with respect to the amount of reducing dopant, the addition ratio of the aromatic ring compound and the reducing dopant preferably ranges from 1 : 20 to 20 : 1 (molar ratio). The light emission luminance of the organic EL element tends to decrease or the life thereof tends to be shortened when the addition ratio of the electron transporting compound and  
20 the reducing dopant is out of this range. Accordingly, the addition ratio of the aromatic ring compound and the reducing dopant more preferably ranges from 1 : 10 to 10 : 1 (molar ratio), and further preferably from 1 : 5 to 5 : 1.

[0068] (electron affinity) In addition, the electron affinity of the electron injection area in  
25 Embodiment Mode 2 preferably ranges from 1.8 to 3.6 eV. When the electron affinity is less than 1.8 eV, electron injection properties tend to decrease, which may cause an increase in driving voltage and a decrease in light emission efficiency. Meanwhile, when the electron affinity is more than 3.6 eV, a complex with low light emission efficiency is easily generated or generation of a blocking junction can be effectively suppressed. Accordingly, the electron  
30 affinity of the electron injection area more preferably ranges from 1.9 to 3.0 eV, and further

preferably from 2.0 to 2.5 eV. In addition, the difference in electron affinity between the electron injection area and the organic light emitting medium is preferably 1.2 eV or less, and more preferably 0.5 eV or less. The smaller the difference in electron affinity is, the easier electron injection from the electron injection area to the organic light emitting medium is, thereby forming an organic EL element capable of high speed response.

[0069] (glass transition point) In addition, the glass transition point (glass transition temperature) of the electron injection area in Embodiment Mode 2 is preferably 100°C or higher, and more preferably 105 to 200°C. By limiting the glass transition point of the electron injection area in this manner, the organic EL element 100 can have an upper temperature limit of 85°C or higher with ease. Thus, even when current flows from the current injection layer to the organic light emitting medium to generate Joule heat in light emission, the tendency of the electron injection area to be damaged in a short time is reduced, leading to longer life of the organic EL element. Note that the glass transition point of the electron injection area can be obtained as a change in specific heat from a specific heat curve that is obtained by heating the components of the electron injection area under the condition of a rate of temperature increase of 10 °C /minute in a nitrogen stream using a differential scanning calorimeter (DSC). This can be applied to other Embodiment Modes and Embodiments.

[0070] (energy gap) In addition, the energy gap (band gap energy) of the electron injection area in Embodiment Mode 2 is preferably 2.7 eV or more, and more preferably 3.0 eV or more. By thus setting the value of energy gap to a predetermined value or more, for example 2.7 eV or more, fewer holes move to the electron injection area across the organic light emitting medium. Accordingly, the efficiency of recombination between holes and electrons is improved, the light emission luminance of the organic EL element increases, and the electron injection area itself can be prevented from emitting light.

[0071] (structure of electron injection area) In addition, the structure of the electron injection area in Embodiment Mode 2 is not specifically limited, and it may be a two-layer structure or a three-layer structure as well as a single layer structure. Further, the thickness of the electron

injection area is not specifically limited, though it preferably ranges, for example, from 0.1 nm to 1  $\mu$ m, and more preferably from 1 to 50 nm.

[0072] (method for forming electron injection area) Next, a method for forming the electron injection area is described. The method for forming the electron injection area is not specifically limited as long as a thin film layer with an even thickness can be formed. For example, a known method such as an evaporation method, a spin coating method, a casting method, and an LB method can be applied. Note that an aromatic ring compound that does not contain a nitrogen atom and a reducing dopant are preferably evaporated at the same time, and this evaporation method is described in detail in Embodiment Mode 3.

[0073] In addition, the electron injection area and the organic light emitting medium are preferably formed by the same method. For example, if the organic light emitting medium is formed by an evaporation method, it is preferable that the electron injection area be also formed by the evaporation method. Such deposition by the same method allows the electron injection area and the organic light emitting medium to be formed continuously, which is advantageous in simplification of equipment and reduction in manufacturing time. Further, since the electron injection area and the organic light emitting medium are rarely oxidized, the light emission luminance of the organic EL element can also be improved.

[0074] [Embodiment Mode 3] Next, Embodiment Mode 3 of the invention is described with reference to FIGS. 3 and 4. Embodiment Mode 3 provides a method for manufacturing a first organic EL element, where the composition ratio of constituent materials can be made uniform even when an organic light emitting layer and the like have a large area, variations in driving voltage of the organic EL element can be reduced, and life homogenization and space savings can be achieved. That is to say, Embodiment Mode 3 provides an evaporation method for an organic EL element thin film layer, where a vacuum evaporation apparatus 201 as shown in FIGS. 3 and 4 is used as an example, and deposition is performed by simultaneously evaporating different evaporation materials from a plurality of evaporation sources 212A to 212F disposed to face a substrate 203. The evaporation method is characterized by providing the substrate 203

with a rotation axis line 213A for rotating the substrate 203, disposing each of the evaporation sources 212A to 212F apart from the rotation axis line 213A of the substrate 203, and evaporating while rotating the substrate 203.

5 [0075] Here, the vacuum evaporation apparatus 201 shown in FIGS. 3 and 4 includes a vacuum chamber 210, a substrate holder 211 for fixing the substrate 203, which is provided at the top of the vacuum chamber 210, and the plurality of (six) evaporation sources 212A to 212F to be filled with evaporation materials, which are provided under the substrate holder 211 so as to face the substrate holder 211. The inside of the vacuum chamber 210 can be maintained under  
10 predetermined reduced pressure by an evacuation means (not shown). Note that although the six evaporation sources are shown in the drawings, the invention is not limited to this, and five or less or seven or more evaporation sources may be provided.

[0076] In addition, the substrate holder 211 includes a holding portion 212 for supporting the  
15 periphery of the substrate 203, and is constituted so as to hold the substrate 203 in a horizontal position in the vacuum chamber 210. A rotation axis portion 213 for rotating (revolving) the substrate 203 is provided in a perpendicular direction at the center of the top surface of the substrate holder 211. The rotation axis portion 213 is connected to a motor 214 that is a rotation drive means. The rotation of the motor 214 rotates the substrate holder 211 as well as  
20 the substrate 203 supported by the substrate holder 211 around the rotation axis portion 213. In other words, the center of the substrate 203 is provided with the rotation axis line 213A in a perpendicular direction by the rotation axis portion 213.

[0077] Specifically described next is a method for forming the organic light emitting layer 16  
25 and the electron injection layer 14 over the substrate 203 using such a vacuum evaporation apparatus 201. First, the plane square substrate 203 as shown in FIG. 2 is prepared and locked in the holding portion 212 of the substrate holder 211 so as to be kept in a horizontal position. The substrate 203 held in a horizontal position shown in FIG. 2 illustrates this state.

30 [0078] Here, on a virtual circle 221, the evaporation sources 212 are respectively filled with a

material for a first organic semiconductor layer, a material for a first inorganic charge-barrier layer, a material for an organic light emitting layer, a material for a second organic semiconductor layer, a material for a second inorganic charge-barrier layer, and a material for a cathode. Then, the pressure of the vacuum chamber 210 is reduced by the evacuation means to a predetermined vacuum level, for example  $1.0 \times 10^{-4}$  Torr. Note that the organic light emitting layer 16 and the like are also preferably formed by evaporating two or more kinds of electron transporting compounds, uniformly evaporating a hole transporting compound and an electron transporting compound in combination, or evaporating compounds so that an electron transporting compound closer to the cathode has a higher concentration than a hole transporting compound.

[0079] Then, each of the evaporation sources 212 is heated to evaporate each constituent material, while the motor 214 is rotated and driven to rotate the substrate 203 around the rotation axis line 213A at a predetermined speed, for example 1 to 100 rpm. In this manner, a plurality of evaporation materials are simultaneously evaporated while rotating the substrate 203, thereby forming the organic light emitting layer 16 and the like.

[0080] In addition, as shown in FIG. 4, the evaporation sources 212B and 212C are provided, for example, at a predetermined distance M from the rotation axis line 213A of the substrate 203 in a horizontal direction. Accordingly, the rotation of the substrate 203 can regularly change the incident angle of the two kinds of evaporation materials to the substrate 203. Thus, the evaporation materials can be uniformly attached to the substrate 203, thereby certainly forming a thin film layer with a uniform composition ratio of evaporation materials, for example a concentration unevenness of  $\pm 10\%$  (molar conversion) in the film surface of the electron injection layer 14. Further, when the evaporation is performed in this manner, the substrate is not required to orbit and space and equipment for the orbit are not necessary; therefore, deposition can be performed with the minimum space and at low cost. Note that the orbit of the substrate means that the substrate is rotated around a rotation axis that is present outside the substrate, and requires a larger space than in the case of the rotation.

[0081] In addition, when the manufacturing method of Embodiment Mode 3 is implemented, the shape of the substrate 203 is not specifically limited. For example, when the substrate 203 is a short side flat plate as shown in FIG. 3, it is desirable that the plurality of evaporation sources 212A to 212F be provided on the circumference of the virtual circle 221 with a center on the rotation axis line 213A of the substrate 203 so that  $M > (1/2) \times L$  is satisfied if the radius of the virtual circle 221 is M and the length of one side of the substrate 203 is L. Note that if each length of the sides of the substrate 203 is not the same but different, the length of the longest side is to be L. According to such a structure, the incident angles of the evaporation materials from the plurality of evaporation sources 212A to 212F to the substrate 203 can be made equal to each other; therefore, the composition ratio of the evaporation materials can be controlled more easily. Further, since such a structure allows the evaporation materials to be evaporated at a constant incident angle with respect to the substrate 203, perpendicular incidence is not performed and the uniformity of the composition ratio in the film surface can be further improved.

[0082] In addition, when the manufacturing method of Embodiment Mode 3 is implemented, it is desirable that each of the evaporation sources 212A to 212F be provided at an angle of  $360^\circ/n$  from the center of the virtual circle 221 as shown in FIG. 3, if the plurality of evaporation sources 212A to 212F are provided on the circumference of the virtual circle 221 with a center on the rotation axis line 213A of the substrate 203, and the number (quantity) of the plurality of evaporation sources 212A to 212F is n. For example, when six evaporation sources 212 are provided, each of them is preferably formed at an angle of  $60^\circ$  from the center of the virtual circle 221. As a result, the plurality of evaporation materials can be deposited on each part of the substrate 203 so as to overlap sequentially, thereby easily forming thin film layers having composition ratios regularly different in the thickness direction of the film.

[0083]

[Embodiment] [Embodiment 1]

(1) Preparation for manufacturing of organic EL element

In order to manufacture an organic EL element of Embodiment 1, first, a transparent electrode film of ITO is formed as an anode layer over a transparent glass substrate with a thickness of 1.1

mm, a longitudinal side of 200 mm, and a lateral side of 200 mm. Then, the glass substrate provided with the anode layer is ultrasonically cleaned in isopropyl alcohol and dried in a N<sub>2</sub> (nitrogen gas) atmosphere, then further cleaned for 10 minutes using UV (ultraviolet) and ozone. Hereinafter, the glass substrate and the anode layer are collectively referred to as a substrate.

5 Subsequently, the cleaned substrate is attached to a substrate holder of a vacuum chamber in a vacuum evaporation apparatus (product of ULVAC Japan, Ltd.), and evaporation sources are respectively filled with a material for an organic semiconductor layer (copper phthalocyanine and DDQ), a material for an inorganic charge-barrier layer (SiO<sub>2</sub>), an organic light emitting layer (DPVTP and DPAVB<sub>i</sub>), a material for an electron injection layer (Alq), and a material for a  
10 cathode layer (aluminum and lithium). Note that the structural formulas of DPVTP, DDQ, and DPAVB<sub>i</sub> are shown in the following formulas (7), (8), and (9) respectively.

[0084]

[Chemical Formula 7]

15

[0085]

[Chemical Formula 8]

[0086]

20 [Chemical Formula 9]

[0087] (2) Manufacturing of organic EL element

After the pressure of the vacuum chamber is reduced to a vacuum level of  $1 \times 10^{-6}$  Torr, a first organic semiconductor layer with a thickness of 600 Å, a first inorganic charge-barrier layer with  
25 a thickness of 50 Å, an organic light emitting layer with a thickness of 400 Å, an electron injection layer with a thickness of 200 Å, and a cathode layer with a thickness of 2000 Å are sequentially stacked over the anode layer formed on the substrate, thereby obtaining an organic EL element. When the first organic semiconductor layer is formed, copper phthalocyanine and DDQ are simultaneously evaporated in accordance with the method described in Embodiment  
30 Mode 3 at a speed of 50 Å/second and a speed of 1 Å/second respectively. When the first

inorganic charge-barrier layer is formed,  $\text{SiO}_x$  ( $1 < x < 2$ ) is evaporated at a speed of 1 Å/second. When the organic light emitting layer is formed, DPVTP and DPAVB<sub>i</sub> are simultaneously evaporated at a speed of 50 Å/second and a speed of 1 Å/second respectively. When the electron injection layer is formed, Alq is evaporated at a speed of 2 Å/second. In addition, when the cathode layer is formed, aluminum and lithium are simultaneously evaporated at a speed of 10 Å/second and a speed of 0.1 Å/second respectively. Note that the organic EL element is manufactured without breaking the vacuum state from the formation of the organic light emitting layer to the formation of the cathode layer.

[0088] (3) Evaluation of organic EL element

A DC voltage of 8 V is applied between the two electrodes provided that the cathode layer of the obtained organic EL element is the negative (-) electrode and the anode layer thereof is the positive (+) electrode. At this time, the current density is 1.8 mA/cm<sup>2</sup>, the light emission luminance is 92 cd/m<sup>2</sup>, and blue light is emitted. In addition, when the obtained organic EL element is driven with a constant current of 10 mA/cm<sup>2</sup>, leakage current is not generated even after 1000 hours.

[0089] [Embodiment 2] In Embodiment 2, an organic EL element is manufactured in the same manner as in Embodiment 1, except that TPDP represented by the following formula (10) (in the formula (10), m and n each are an integer of 1 to 10) and iron chloride (weight ratio 100 : 5) are used instead of copper phthalocyanine and DDQ used for the organic semiconductor layer in Embodiment 1. Then, a DC voltage of 8 V is applied to evaluate the light emitting state. As a result, the current density is 1.6 mA/cm<sup>2</sup>, the light emission luminance is 82 cd/m<sup>2</sup> at this time, and blue light is emitted. In addition, when the obtained organic EL element is driven with a constant current of 10 mA/cm<sup>2</sup>, leakage current is not generated even after 1000 hours.

[0090]

[Chemical Formula 10]

[0091] [Embodiment 3] In embodiment 3, an organic EL element is manufactured in the same

manner as in Embodiment 1, except that PMMA as a binder and antimony-doped tin oxide as conductive particles (weight ratio 1 : 1) are used instead of copper phthalocyanine and TCNQ used for the organic semiconductor layer in Embodiment 1. Then, a DC voltage of 8 V is applied to evaluate the light emitting state. As a result, the current density is 1.5 mA/cm<sup>2</sup>, the light emission luminance is 76 cd/m<sup>2</sup> at this time, and blue light is emitted. In addition, when the obtained organic EL element is driven with a constant current of 10 mA/cm<sup>2</sup>, leakage current is not generated even after 1000 hours.

[0092] [Embodiment 4] In Embodiment 4, an organic EL element is manufactured in the same manner as in Embodiment 1, except that Li<sub>2</sub>O is evaporated to have a thickness of 10 Å instead of Alq used for the electron injection layer in Embodiment 1 and phthalocyanine and Li are simultaneously evaporated at a speed of 20 Å/cm<sup>2</sup> so as to have a thickness of 200 Å. Then, a DC voltage of 8 V is applied to evaluate the light emitting state. As a result, the current density is 1.7 mA/cm<sup>2</sup>, the light emission luminance is 83 cd/m<sup>2</sup> at this time, and blue light is emitted. In addition, when the obtained organic EL element is driven with a constant current of 10 mA/cm<sup>2</sup>, leakage current is not generated even after 1000 hours.

[0093] [Comparative Example 1] In Comparative Example 1, an organic EL element is manufactured in the same manner as in Embodiment 1, except that the organic charge-barrier layer in Embodiment 1 is not provided. Then, a DC voltage of 8 V is applied to evaluate the light emitting state. As a result, the current density is 2.2 mA/cm<sup>2</sup>, the light emission luminance is 41 cd/m<sup>2</sup> at this time, and blue light is emitted. In addition, when the obtained organic EL element is driven with a constant current of 10 mA/cm<sup>2</sup>, leakage current is generated after 1000 hours, and the voltage rises to 11 V.

[0094] [Comparative Example 2] In Comparative Example 2, an organic EL element is manufactured in the same manner as in Embodiment 1, except that DDQ used with copper phthalocyanine in Embodiment 1 is not used and the organic semiconductor layer is not formed. Then, a DC voltage of 8 V is applied to evaluate the light emitting state. As a result, the current density is significantly reduced to as low as 0.7 mA/cm<sup>2</sup>, the light emission luminance is 30

cd/m<sup>2</sup> at this time, and blue light is emitted. In addition, when the obtained organic EL element is driven with a constant current of 10 mA/cm<sup>2</sup>, leakage current is not generated even after 1000 hours.

5 [0095]

[Effect of the Invention] As specifically described above, according to the organic EL element of the invention, improvement in light emission efficiency (as an example, a light emission luminance of 30 cd/m<sup>2</sup> or more) in low voltage drive (as an example, a DC voltage of 7 V or less) can be achieved by oxidizing an organic light emitting substance around the interface with an anode layer using an oxidizing dopant and the like.

10 [0096] In addition, according to the method for manufacturing an organic EL element of the invention, a step of oxidizing an organic light emitting substance around the interface with an anode layer is included. As a result, an organic EL element with high light emission efficiency (as an example, a light emission luminance of 30 cd/m<sup>2</sup> or more) can be effectively provided in low voltage drive (as an example, a DC voltage of 7 V or less).

#### [Brief Description of Drawings]

FIG. 1 is a cross sectional view of an organic EL element in Embodiment Mode 1.

20 FIG. 2 is a cross sectional view of an organic EL element in Embodiment Mode 2.

FIG. 3 is a perspective view of a vacuum evaporation apparatus in Embodiment Mode 3.

FIG. 4 is a cross sectional view of a vacuum evaporation apparatus in Embodiment Mode 3.

FIG. 5 is a cross sectional view of a conventional organic EL element (part 1).

FIG. 6 is a cross sectional view of a conventional organic EL element (part 2).

25

#### [Description of Reference Numerals]

10: anode layer 12: first organic semiconductor layer 14: first inorganic charge-barrier layer

16: organic light emitting layer 18: second inorganic charge-barrier layer 20: second organic

semiconductor layer 22: cathode layer 24: electron injection layer 100, 102: organic EL

30 element 201: vacuum evaporation apparatus 203: substrate 210: vacuum chamber 211:

substrate holder 212: holding portion 212A to 212F: evaporation sources 213: rotation axis  
portion 213A: rotation axis line 214: motor 221: virtual circle